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(54) Title: MICROSTRUCTURED MEMBRANES AND METHODS FOR MAKING SAME
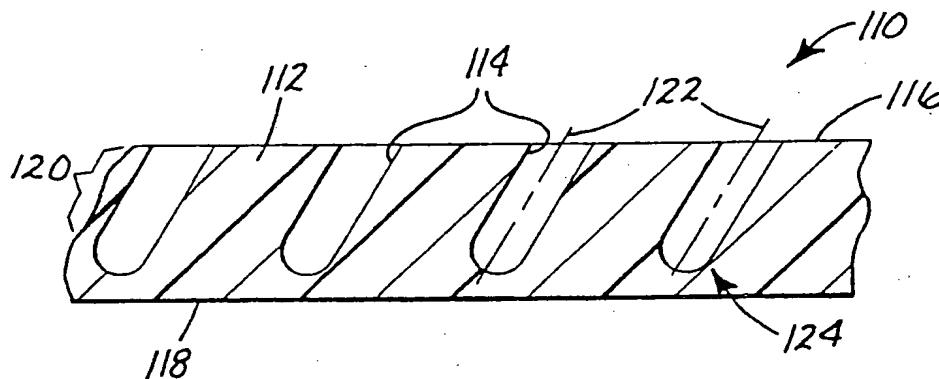
(57) Abstract

Microstructured membrane comprising a sheet having first and second faces with an array of pores extending into the sheet from the first face, and in some instances extending through the entirety of the sheet. Substantially each pore within the array is individually surrounded by a flat land area and the major portion of the walls of each pore are substantially parallel to the longitudinal axis of the pore. The pores have an average characteristic dimension of between about 0.1 and about 5000 microns and a pore size distribution of less than about 10 percent, the longitudinal axes of pores within the array being substantially parallel with each other. Also, articles incorporating such membranes and methods for making such membranes.

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MICROSTRUCTURED MEMBRANES
AND
METHODS FOR MAKING SAME

Field of Invention

5   The present invention relates to
microstructured membranes having arrays of defined
pores therein, articles incorporating such membranes,
10   and methods for making such membranes.

Background

          Certain types of microstructured membranes with
a plurality of cavities and orifices therein are known.
15   U.S. Patent No. 2,345,080 (Von Ardenne)
discloses production of filters by perforating a foil
with ion rays. U.S. Patent No. 3,303,085 (Price et
al.) discloses formation of molecular sieves utilizing
charged particle radiation. U.S. Patent No. 3,612,871
20   (Crawford et al.) discloses a method for treating
plastic film by charged particle irradiation and then
treatment with a selected solvent to leave
substantially cylindrical holes in the film.
          U.S. Patent No. 4,044,222 (Kestenbaum)
25   discloses a method of forming tapered apertures in thin
films.
          U.S. Patent No. 4,092,515 (Joslin et al.)
discloses a method of drilling a hole in a workpiece,
the hole being substantially free of a recast layer,
30   the method comprising laser irradiation of a workpiece
in an oxidizing environment. U.S. Patent No. 4,262,186
(Provancher) discloses a process for forming holes in a
substrate employing laser perforation of a chemical
mask, chemical etching of the substrate through the
35   perforated mask, and then removing the mask to yield
the substrate with holes therein. U.S. Patent No.
4,855,049 (Toulemonde et al.) discloses formation of
porous membranes by irradiation of a film from two
sides with ionizing radiation and chemical etching.

U.S. Patent No. 4,652,412 (Chiulli) discloses a
method for forming a microporous filter by embossing
holes in an embossable polymer on a porous support.

Surface relief patterns and holes through films
5   have been formed by methods utilizing laser
irradiation. For instance, U.S. Patent No. 4,402,571
(Cowan et al.) discloses a method for producing a
surface relief pattern utilizing laser interferometry.
U.S. Patent No. 4,496,216 (Cowan) discloses formation
10   of circular holes in photosensitive material utilizing
exposure to at least three coherent beams of radiation.

U.S. Patent No. 4,923,608 (Flottman et al.)
discloses membranes having tapered or rounded
funnel-shaped pores with fixed pore size and a pore
15   size distribution of less than 10 percent. The
dividers between the pores are saddle-like and are of
two different heights. The average pore diameters are
said to range from 0.05 to 10 microns. The membranes
are manufactured through erosion of pores using one or
20   more intensity modulated laser beams projected onto a
substrate.

U.S. Patent No. 4,032,743 (Erbach et al.)
discloses a laser microperforator.

25   Summary of Invention
The present invention provides novel
microstructured membranes having an array of pores
therein, articles incorporating such membranes, and
novel methods for making such membranes.
30   In brief summary, membranes of the invention
comprise a sheet having first and second major faces
with at least one array of pores that extend into the
sheet from the first face. Depending upon the
embodiment, the pores may be cavities that extend only
35   partially through the sheet or the pores may be
orifices that extend completely through the sheet,
i.e., such that they open through both the first and

second major faces. At least 50 percent and preferably
at least 75 percent of the length of the walls of each
pore within a given array are straight. The land areas
between pore openings are flat, i.e., divider portions
between adjacent pores are of uniform height such that
the distance between the first and second major faces
is equal. In some embodiments, a major portion, i.e.,
at least 50 percent and preferably at least 75 percent
of the length, of the walls of each pore within a given
array are substantially parallel to the longitudinal
axis of the pore. Typically, the pores have an average
characteristic dimension of between about 0.1 and about
5000 microns and the pores within a given array are
substantially uniform in size with a characteristic
dimension distribution of about ± 10 percent or less
about the average pore size. Also, the pores within a
given array have substantially uniform orientation,
with the longitudinal axes of the pores being
substantially parallel, i.e., a deviation of less than
about 5°, with each other.

Membranes of the invention differ from those
previously available in a number of ways including but
not limited to the following:

a) the pores within a given array can exhibit a
   degree of uniformity of size, shape, and/or
   orientation that was previously unattainable;

b) the pores can have desired shapes, sizes, and
   depth (i.e., in the case of cavities) and can be
   arranged in geometries not previously attainable;

c) the pores can be formed in membranes made of
   materials in which such pores could not
   previously be formed;

d) the membrane can exhibit a degree of side to side
   uniformity that was previously either not
   attainable or not readily attainable; and

e) the land areas between pore openings are flat.

As a result of their novel features, membranes of the
invention provide unexpected and/or previously
unattained advantages and utility.

Briefly summarizing, one novel method for
making membranes of the invention comprises:

    a) providing a mask with an array of apertures
       therein, the apertures being of the desired
       surface shape and size of the pores and being
       arranged in the pattern in which the pores are
       desired;

    b) positioning the mask in close proximity,
       preferably in contact, with the first face of the
       film from which the membrane is to be made; and

    c) forming an array of pores simultaneously in the
       film by application of directional means of
       boring through the mask, e.g., ablation or
       etching;

to yield a membrane with an array of pores therein.

Membranes of the invention may be used for a
variety of purposes with advantageous results. For
instance, they may be used as filter media, articles
with microstructured surfaces, etc. Membranes of the
invention may be substantially flat or may be non-
planar as desired.

Brief Description of Drawing

The invention will be further explained with
reference to the drawing, wherein:

Figure 1 is an illustration of a cross-section
of a portion of one embodiment of a microstructured
membrane with orifices of the invention;

Figure 2 is an illustration of a cross-section
of a portion of another embodiment of a microstructured
membrane with cavities of the invention;

Figure 3 is an illustration of a cross-section
of a portion of another embodiment of a microstructured
membrane of the invention;

Figure 4 is a scanning electron microscope
photograph of the membrane fabricated in Example 1; and

Figures 5a-5d are a series of illustrations of
a cross-section of a portion of a sheet during the
process of making a membrane of the invention as
described in Example 13.

These figures, which except for Figure 4 are
idealized and not to scale, are intended to be merely
illustrative and non-limiting.

Detailed Description of Illustrative Embodiments

Figure 1 shows an illustrative embodiment of a
membrane of the invention wherein membrane 10 comprises
sheet 12 with pores 14 therein. In the embodiment
shown, pores 14 open in first face 16 of sheet 12 and
extend through the entirety of sheet 12 to open through
second face 18 also. Pores which extend through the
entirety of the sheet are sometimes referred to herein
as orifices.

Another illustrative embodiment is shown in
Figure 2 wherein membrane 110 comprises sheet 112 and
pores 114 that open in first face 116 of sheet 112 but
extend through only a portion of sheet 112 and do not
open through second face 118 thereof. Such pores are
sometimes referred to herein as cavities. Membranes
may be made with two or more arrays of cavities having
varying depth if desired.

An additional feature of some embodiments is
that, referring to Figure 2, major portion 120 of the
walls of each opening 114 are substantially parallel to
longitudinal axis 122 of opening 114. As used herein,
"longitudinal axis" refers to the axis of the pore
extending from the first face of the membrane into the
sheet. The longitudinal axis of the openings in a
membrane of the invention is generally parallel to the
axis of application of the directional means for boring
by which the openings are formed. By "substantially

parallel" it is meant that the deviation between the
major portion of the wall of each opening and the
longitudinal axis is less than about 5°. Accordingly,
in these embodiments a pore has a substantially uniform
5 cross-sectional area throughout at least the portion
defined by the major portions of its walls. As used
herein, "cross-sectional area" refers to the area of a
geometric surface on a plane perpendicular to the
longitudinal axis of the pore and bounded by the
10 intersection of the plane with the walls of the
opening.

In membranes of the invention, the major
portion, i.e., at least 50 percent and typically
preferably at least 75 percent, of the length of the
15 walls of each pore beginning at the edge of the opening
in the first face of the sheet and extending into the
sheet are substantially straight. Explained in another
way, the regions of intersection with the walls or
sides of a pore of any plane parallel to and
20 intersecting the longitudinal axis of the pore are
straight lines for at least 50 percent and typically
preferably at least 75 percent of the length of the
regions of intersection beginning at the edge of the
pore's opening in the first face of the sheet.

25 In the case of cavities, the second end of the
pore, i.e., the end opposite the end that opens in the
first face of the membrane is typically somewhat
tapered or rounded. Referring to Figure 2, this second
end is referred to herein as foot 124. Depending upon
30 the characteristics of the means of boring employed and
the characteristics of the film, the foot may exhibit
string-like features or nodules, cones, or other
irregularities sometimes referred to as artifacts.
Dyer, Jenkins, and Sidhu, Development And Origin Of
35 Conical Structures On XeCl Laser Ablated Polyimide,
Applied Physics Lett., V. 49, Iss. 8, pp 453-55, 1986,

suggests that such artifacts may be due to impurities
in the sheet from which the membrane is being made.

Membranes of the invention may be made with
pores having an average "characteristic dimension" of
desired size. As used herein, "characteristic
dimension" means the largest cross-sectional dimension
of the pore in a plane perpendicular to the
longitudinal axis of the pore. Typically, the average
characteristic dimension of pores in membranes of the
invention is between about 0.1 and about 1000 microns.
An advantage of the present invention is that the
membrane may have, within a given array of pores, a
pore size distribution at the first face of the sheet
of less than about 10 percent and sometimes less than 5
percent. As used herein, "pore size distribution"
means the standard deviation of the average
characteristic dimension. Similar size distributions
may be achieved for the openings on the second face of
the sheet for orifices.

Membranes of the invention may be made with
pores having a variety of shapes, i.e., cross-sectional
profile of the pore as the region of a plane
perpendicular to longitudinal axis of the pores bounded
by the pore walls. For instance, by selection of a
suitable mask, pores may have a cross-sectional profile
that is circular, ovate, rectangular, triangular, some
other polygon, or irregular shapes.

Membranes of the invention may be made with a
desired density of pores. Typically, the first face of
the membrane may have a surface porosity of at least
about 0.01 percent, sometimes at least about 5 percent,
and if desired at least about 20 percent or more. By
selection of pore shape and orientation, membranes of
the invention may be made with very high surface
porosity, e.g., up to about 75 percent or even 95
percent. As used herein, "surface porosity" is the
percentage of the area of the face of the membrane

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where the film material has been bored away to yield
the pores. It will be understood that as surface
porosity increases, the structural strength of the
resultant membrane decreases.

5   Membranes of the invention may be made from
films of many types including polymeric materials,
glass, ceramics, and metals. As discussed below,
selection of the film material and selection of the
boring means are dependent in part upon one another.

10   In general, ultraviolet boring techniques,
e.g., ablation, may be used with polymeric films that
contain unsaturated bonds. Membranes may be made using
ultraviolet boring techniques with other polymers by
incorporating ultraviolet absorbers therein to render

15   the film ablative. Illustrative examples of polymeric
film materials which may used to make membranes of the
invention using ultraviolet ablative techniques
include: polyvinyls such as acrylics and methacrylics,
polyynes, polyenes (e.g., polyethylene, polypropylene,

20   and polystyrene), polydienes (e.g., polybutadiene and
polyisoprene), polyesters (e.g., terephthalate esters,
etc.), polyurethanes, polyamides (e.g., nylons),
polyimides, polyethers, etc. Some polymeric materials
inherently exhibit sufficient ultraviolet absorption to

25   be subject to ultraviolet-induced ablation.
Ultraviolet sensitizing agents may need to be
incorporated into other polymeric materials in order to
render them sufficiently subject to ultraviolet-induced
ablation. Such agents are well known and may be

30   readily selected and used by those with ordinary skill
in the art.
          Ultraviolet ablation techniques may also be
used to make membranes of the invention from sheets of
some types of glass. Reactive ion etching techniques

35   may be used to make membranes of the invention from
sheets of some types of polymers, glass, ceramics, and
metals.

Selection of the film material may also be made
in light of the intended application of the membrane.
For instance, many different nylons may be used where a
relatively hydrophilic membrane is desired and

5   polyethylene terephthalate may be used where a
relatively hydrophobic membrane is desired.

Membranes of the invention may be made from
rigid or flexible film materials as desired. For
instance, polymeric membranes which can be wrapped

10   around a 1 millimeter diameter mandrel without breaking
can be made if desired.

An advantage of the present invention is that
pores may be made in very thick films and in a variety
of aspect ratios. Membranes of the invention may be

15   made in a variety of thicknesses as desired, depending
in many instances upon the application for which the
membrane is being prepared. For example, membranes of
the invention may be made from films having thicknesses
of up to about 5000 microns. Also, membranes may be

20   made with pores having very low aspect ratios, e.g.,
1:100, or up to very high aspect ratios, e.g., 60:1.
As used herein, "aspect ratio" refers to the ratio of
(1) the interior length of the longitudinal axis of the
pores, i.e., the portion of the longitudinal axis which

25   is within the volume of film vacated during boring of
the pores, to (2) the average characteristic dimension
of the pores at the first face of the film.

An advantage of the highly uniform pore size
and narrow distribution of pore size which can be

30   achieved in membranes of the invention is that the
resultant membranes can exhibit highly uniform
characteristics. For instance, in the case of a
membrane wherein the pores extend completely through
the sheet, the membrane can be used as a filter which

35   provides uniform separation properties across its
entir ty. In such embodiments, where the pores have
substantially uniform cross-sectional areas along their

full length, both sides of the membrane exhibit uniform properties. For example, filtration performance and flexural strength are substantially equal from either face of the membrane.

5   In some embodiments, membranes may be made wherein the walls of the pores define frustum-like shapes. In such instances, each pore does not have a uniform cross-sectional area and the major portions of the walls of each pore are not substantially parallel

10   to the pore's longitudinal axis. Figure 3 illustrates membrane 210 comprising sheet 212 with pores 214 therein extending from first face 216 through second face 218. Major portions 220 of pores 214 are not parallel to each other or to longitudinal axis 222.

15   For instance, pores may be made which have average characteristic dimensions at their largest end of between about 0.1 and about 5000 microns. As with other embodiments of the invention, however, at least 50 percent and preferably at least 75 percent of the

20   length of the walls of each pore within a given array are straight. An advantage of such membranes is that they offer greater strength than do membranes with pores with similar minimum cross-sectional areas but having non-linear walls or wherein the dividers between

25   adjacent pores are saddle-shaped. Some embodiments of such pores are sometimes referred to as being "Gaussian-shaped". Filter membranes with frustum-like orifices exhibit less tendency to clog when the stream being filtered enters the face of the membrane having

30   the smaller ends of the orifices.

       In some embodiments, membranes of the invention will comprise two or more arrays of different pores as described herein wherein the pores in different arrays have different characteristics. The arrays may be

35   located at separate areas of the membrane or may be partially or totally superimposed.

An advantage of membranes of the invention is
that the portions of the first face between pores,
referred to herein as "land areas", and the land areas
in the second face in those embodiments wherein the
pores extend completely through the membrane, are
substantially planar or flat. In comparison, the
membranes disclosed in U.S. Patent No. 4,923,608 have
saddle-like contours on the surface which would be
subject to greater tendency to clog and exhibit more
difficulty in backwashing and clearing than would
filter membranes of the invention. In a tangential
flow of fluid across either face of membranes of the
invention, the lack of surface saddle-like structures
will allow for a better sweep of the fluid across the
surface and facilitate removal of filter cakes.
Furthermore, membranes having saddle-like dividers
between pores exhibit reduced flexural strength as
compared to membranes of the invention.

In general, the methods for making membranes of
the invention comprise:

a) providing a mask comprising a sheet with an array
of apertures therein, the apertures being of the
diameter and shape of the desired pores and being
arranged in a pattern corresponding to that
desired of the pores;

b) positioning the mask in close proximity to,
preferably in intimate contact with, the first
face of a film from which the membrane is to be
formed; and

c) forming an array of pores simultaneously in the
film by application of directional means for
boring through the mask;

to yield the membrane with the array of pores therein.

Selection of means for boring will be based in
part upon the nature of the mask used, the
characteristics of the film from which the membrane is
being made, and the features desired of the pores.

Illustrative examples of means for boring include
application of a collimated stream of reactive ions,
plasma, or collimated energy beam (e.g., excimer laser
or ultraviolet beam). In addition to being highly

5   directional, the means for boring is preferably one
which substantially does not deform the sheet outside
the area being bored, i.e., one which substantially
causes only localized removal of sheet material in the
desired location and not in the surrounding land areas.

10   For this reason, conventional chemical etching is
typically not desired for use in the present invention
because it typically does not exhibit the desired
directional boring. Preferably, by-products produced
during boring, e.g., ablation by-products, are removed

15   during boring such as by ventilation.
          In some embodiments, the mask is placed in
proximity, preferably in intimate contact, with the
film after the mask is generated.
          In other embodiments, the mask is generated

20   from a precursor material in direct contact with the
film. For instance, a mask may be generated by
     a) applying a layer of resist material to the first
        face of the film from which a membrane is to be
        made;

25   b) imagewise exposing the layer of resist material
        with actinic radiation to differentially harden
        it;
     c) removing the unhardened areas of the layer of
        resist material, exposing first areas of the

30   first face of the film, the remaining, i.e.,
        second areas of the first face remaining covered;
     d) applying a cap coating to the exposed first areas
        of the first face and the remaining portions of
        the layer of resist material;

35   e) removing the remaining portions of the resist
        material and the cap coating thereon, thereby

exposing the second areas of the first face of
the film.

The resist material can be imagewise exposed
with a number of techniques, including selective
scanning with a beam of suitable radiation, e.g., a
laser beam of selected wavelength. In another
technique, the imagewise exposure is performed with
laser interferometry.

Examples

The invention will be further explained by the
following illustrative examples which are intended to
be nonlimiting.

In Examples 1 and 4 image analysis was
performed utilizing an IBAS Image Analyzer with a 10X
objective, 6.3X ocular, and green light filter to
characterize the structure of the membrane and its
constituent elements. All area ("Area"), diagonal
("D_{diag}"), and edge ("D_{edge}") dimension measurements were
determined using the darkest continuous line of the
aperture image. Area measurements were based on
standard area determination criteria common to image
analysis equipment and software. Diagonal and edge
image dimension measurements were obtained by commonly
utilized feret or caliper measurement techniques.
Results for Area, D_{diag}, and D_{edge} determinations along
with the calculated D_{diag}/D_{edge} ratio, referred to herein
as the shape factor, which should be 1.4142 for a
perfect square where D_{diag} is the diagonal of the square,
and D_{edge} is the edge length for a square having the same
area as the measured area, for the incident (Sample I)
and exit (Sample E) membrane surface images was
determined as shown below. In Example 13 the same
device was used to determine the average diameter of
the orifices formed.

Example 1

A stainless steel mask with uniformly
distributed square apertures was placed in contact with
a 12.2 micron (0.48 mil) thick poly(ethylene
5   terephthalate) (i.e., "PET"), MYLAR^{TM} film (from E.I.
duPont de Nemours). The sides of the apertures were 53
microns in length with, according to the manufacturer,
a standard deviation of about 10 percent and about 35
percent of the mask was open area.

10   The beam from a krypton/fluorine ("KrF")
excimer laser producing 249 nanometer ("nm") radiation
at a pulse frequency of 40 Hertz ("Hz") and pulse
duration of 27 nanoseconds was projected through an
iris and a series of lenses onto the mask. The iris
15   was located about 30.5 centimeters ("cm") from the
laser window and a few cm from the first lens. Three
lenses from ESCO Products Company and made of CORNING^{TM}
7490-UV, a material transparent to light at a
wavelength of 249 nm, with AR-MgF$_2$ antireflective
20   coatings including (1) a 106.7 cm focal length
converging lens located about 108 cm (42.5 inches) from
the PET film plane, (2) a 20.3 cm focal length
diverging lens located about 73 cm (28 3/4 inches) from
the PET film plane, and (3) a 3.4 cm focal length
25   cylindrical lens located about 4 cm (1.5 inches) from
the film plane were used.

Ablation was accomplished by shadowing the mask
pattern onto the PET film. The intensity of the laser
radiation incident to the surface of the film was about
30   200 millijoules per centimeter^2 ("mJ/cm^2") with a beam
shape at the surface of a rectangle about 3 millimeters
(120 mils) wide and 15.2 cm (6 inches) long. The mask
and PET film were moved in register across the middle
10.2 cm (4 inches) of the beam at a rate of about 0.25
35   cm/minute.

Scanning the mask/film combination yielded a
10.2 cm wide PET membrane with pores penetrating

through the membrane. The axes of these pores were
parallel to one another and perpendicular to the
membrane surfaces. The sides of the openings of the
square pores on the face of the sheet to which the
laser was incident had an average length of 51.1
microns with a standard deviation of about 4 percent
and the sides of the opening at the opposite face had
an average length of 52.1 microns with a standard
deviation of about 4 percent as determined by image
analysis. Results for Area D_{diag}, and D_{edge}
determinations (with standard deviation in parentheses)
was as follows:

Sample	Area micron^2	D_{diag} microns	D_{edge} microns	Shape Factor	D_{area} microns
I	2459	67.8 (2.4)	51.1 (2.0)	1.326	49.6 (1.4)
E	2594	69.4 (2.1)	52.1 (1.9)	1.332	50.9 (1.4)

Within the absolute deviation of $\pm$ 2.0 microns for D_{diag}
and $\pm$ 1.9 microns for D_{edge}, orifice dimensions on the
incident and exit faces of the membrane are considered
statistically identical.

        Thus the sizes of either end of the replicated
pores were the same within the statistical distribution
of these dimensions. The sizes of the replicated pores
were also within the statistical distribution of sizes
of the apertures in the mask.

Example 2

        A membrane was prepared as in Example 1 except
a nickel mask having 5 micron diameter round apertures
having a standard deviation of 10 percent and 0.2
percent open area (from PA Technologies) was
substituted for the stainless steel mask.

        A membrane having an array of 5 micron wide
round pores was produced by exposure to a 500 mJ laser
output at 45 Hz.

Example 3

A membrane was prepared as in Example 1 except the mask contained square apertures 20 microns wide having a standard deviation of 10 percent and had an open area of about 35 percent.

A membrane having an array of square pores with 20 micron sides was produced upon exposure to a 500 mJ laser output at 30 Hz.

Example 4

A membrane was prepared as in Example 1 except the mask contained square apertures 106 micron wide having a standard deviation of 10 percent with a square cross section and an open area of about 35 percent.

A membrane having an array of 106 micron pores was produced by exposure to a 500 mJ laser output at 45 Hz. Results for Area, D_{diag}, and D_{edge} determinations along with the calculated Shape Factor, and D_{area} for the incident (Sample I) and exit (Sample E) membrane surface images was as follows:

Sample	Area micron^2	D_{ding} microns	D_{edge} microns	Shape Factor	D_{area} microns
I	10722	144.0 (3.2)	104.8 (3.2)	1.375	103.5 (2.2)
E	10426	143.5 (3.5)	102.8 (3.6)	1.397	102.1 (2.4)

Within the absolute deviation of ± 3.2 microns for D_{diag} and ± 3.5 microns for D_{edge}, orifice dimensions on the incident and exit faces of the membrane are considered statistically identical.

Example 5

A membrane was prepared as in Example 4 except the PET film employed was about 102 microns thick.

A membrane having an array of 106 micron pores was produced by exposure to a 500 mJ laser output at 50 Hz.

<u>Example 6</u>

A membrane was prepared as in Example 1 except
a 102 micron PET film was substituted for the 12.2
micron (0.48 mil) film.

5   A membrane having an array of regularly spaced
square cavities 53 microns wide and having a depth of
about 40 microns was produced by exposure to a 450 mJ
laser output at 8 Hz.

10   <u>Example 7</u>

A sample was prepared as in Example 4 except a
102 micron PET film was substituted for the 12.2 micron
film.

A membrane having an array of regularly spaced
15   square cavities 106 microns wide and having a depth of
about 40 microns was produced by exposure to a 500 mJ
laser output at 8 Hz.

<u>Example 8</u>

20   A membrane was prepared as in Example 1 except
a 102 micron PET film was substituted for the 12.2
micron film and a mask containing 212 micron apertures
having a standard deviation of 10 percent with a square
cross section and an open area of about 35 percent was
25   substituted for the 53 micron mask.

A membrane having an array of regularly spaced
square cavities 212 microns wide and having a depth of
about 40 microns was produced by exposure to a 500 mJ
laser output at 10 Hz.

30

<u>Example 9</u>

A membrane was prepared as in Example 1 except
a 178 micron PET film was substituted for the 12.2
micron film.

35   A membrane having an array of regularly spaced
square cavities 53 microns wide and having a depth of

about 100 microns was produced by exposure to a 450 mJ
laser output at 21 Hz.

Example 10

A membrane was prepared as in Example 4 except
a 356 micron PET film was substituted for the 12.2
micron film.

A membrane having an array of regularly spaced
square cavities 106 microns wide and having a depth of
about 300 microns was produced by exposure to a 500 mJ
laser output at 50 Hz.

Example 11

A membrane was prepared as in Example 1 except
a 50.8 micron KAPTON^{TM} polyimide film (from duPont) was
substituted for the PET film.

A membrane having a regularly spaced array of
53 micron square pores was produced by exposure to a
500 mJ laser output at 35 Hz.

Example 12

A membrane was prepared as in Example 1 except
a 15.24 micron DARTEK^{TM} Nylon 66 film (from duPont) was
substituted for the PET film.

A membrane having an array of regularly spaced
53 micron square pores was produced by exposure to a
460 mJ laser output at 34 Hz.

Example 13

A 5 micron thick biaxially-oriented PET film
having a surface roughness of 0.1 micron or less was
clamped between a pair of flat frame members, each
member having a circular opening of approximately 2 cm,
with one member fitted with a circular rubber gasket to
facilitate securing the film between the frame members.
The PET film was then stretched by positioning the
circular opening of the frame members over a beveled

cylinder having a diameter slightly smaller than the
opening and applying uniform radial pressure to the
assembly. A flat circular copper gasket was adhered to
the stretched film using a UV curable adhesive

5   (NORLAND^TM 61 Epoxy from Norland Co.). After curing
the adhesive, the film/gasket construction was removed
from the frame assembly by cutting the film along the
outside perimeter of the gasket.

        The PET film was cleaned by immersing the

10   film/gasket construction in a series of three
ultrasonic cleaning baths (about 15 minutes in each
bath) including an 0.1 percent aqueous detergent
solution (LIQUI-NOX^TM soap from Alconox, Inc.), acetone
and isopropyl alcohol ("IPA"). The film was rinsed

15   with ultrapure water, generated by passing tap water
through a Barnstead "NANOpure^TM II" water purification
unit (from Barnstead, a division of Sybron Corp.) for
15 minutes after each bath. After the final rinse with
ultrapure water the film was dried in a stream of pure

20   nitrogen. Subsequent processing of the film to produce
the porous membrane is illustrated in Figures 5a-5d.

        A 0.6 micron thick positive photoresist coating
(1400-17 SHIPLEY^TM from Shipley), was applied to the
clean, dry film in a spin coater apparatus and a

25   pattern developed on the resist coating through two
exposures to laser irradiation. The apparatus, which
utilized Lloyd's mirror fringes phenomena (discussed by
X. Mai, R. S. Moshrefzadeh, U. J. Gibson, G. I.
Stegeman and C. T. Seaton in "Simple Versatile Method

30   for Fabricating Guided-Wave Gratings," Applied Optics,
vol. 24, No. 19, 1985), was equipped with a
helium/cadmium ("HeCd") laser (from Liconix) operating
at 442 nm, an electronic shutter to control exposure
time, a spatial filter (from Jodon) which filtered out

35   the high frequency components of the beam and
collimated the beam to the desired size, and a
sample/mirror assembly comprising a flat mirror

configured at 90° to the sample holder. The mirror had
a flatness of lambda/40.

5   The resist-coated film/gasket assembly was
mounted on the sample holder such that half of the
incident laser beam illuminated the resist coating
directly and the other half of the beam was reflected
onto the coating by the mirror. An interference
between the two portions of the beam created a periodic
interference pattern in the resist coating.

10   Periodicity of the pattern was controlled by adjusting
the angle alpha between the mirror and the incident
beam. The period was calculated using the formula:

$$P = lambda/(2 \text{ sine } alpha)$$

where P is the eventual pore period and lambda is the
15   laser wavelength (442 nm). Prior to the second
exposure, the resist coated film was rotated 90° on the
sample holder.

Figure 5a illustrates film 312 with resist
coating 330 thereon. Following exposure, resist
20   coating 330 has unexposed areas 332 and exposed areas
334.

After the second exposure, the resist layer was
developed for 30 seconds in a 1:4 solution of SHIPLEY™
Developer 351 (from Shipley) in ultrapure water to
25   remove unexposed resist. The resulting developed
structure consisted of an array of regularly spaced
posts 332 of hardened resist coating on the film. A
0.1 micron thick titanium ("Ti") coating was vapor
coated onto the developed structure in a vacuum chamber
30   using Ti vapor and directional coating techniques.
Divergence of the coating beam was approximately 10°
and the film was placed approximately 100 cm from the
Ti boat. Figure 5b illustrates the resultant
intermediate of film 312 with unexposed posts 332 of
35   the resist coating and titanium coating 336 thereon.
The intermediate was then placed in an ultrasonic bath
containing acetone for a few minutes to dissolve the

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posts, leaving the underlying areas of the film exposed.

Directional etching of the film using reactive ion etching ("RIE") with oxygen for two hours at 200 watts and an oxygen pressure of about 30 millitorrs followed by chemical wet etching with a mixture of 50 parts by volume of a 5 weight percent aqueous solution of ethylenediamine tetraacetic acid ("EDTA"), 4 parts by volume of ammonium hydroxide, and 10 parts by volume of a 30 weight percent aqueous solution of hydrogen peroxide to remove the Ti mask yielded a microporous membrane. Figure 5c illustrates application of RIE beam 338 to the exposed areas of film 312 with the remaining portions of titanium coating 336 serving as a mask. Figure 5d illustrates membrane 310 with pores 314 following completion of RIE and removal of the titanium mask. Image analysis of the resultant membrane indicated the orifices had an average characteristic dimension of 0.7058 ± 0.0794 microns.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention.

Claims:

1.   A microstructured membrane comprising a
sheet having a first major face and a second major face
5   with an array of pores extending into said sheet from
said first face characterized in that substantially
each pore within said array is individually surrounded
by a flat land area, said pores having an average
characteristic dimension of between about 0.1 and about
10   5000 microns and a pore size distribution of less than
about 10 percent, the longitudinal axes of said pores
being substantially parallel with each other.

2.   The membrane of claim 1 further
15   characterized in at least one of the following:
        a) said sheet comprises one or more of the following:
           glass, ceramic, metal, or polymer; or
        b) said sheet is made of a material that is subject
           to directional ablation by exposure to ablative
20   radiation or reactive ion etching; or
        c) said sheet comprises one or more of the following:
           polyvinyls, polyynes, polyenes, polydienes,
           polyesters, polyurethanes, polyamides, polyimides,
           polyethers, and polycarbonates.
25

3.   The membrane of claim 1 further
characterized in at least one of the following:
        a) said sheet is less than about 50 microns thick; or
        b) said sheet has a thickness greater than about 50
30   microns; or
        c) said sheet has a thickness up to about 5000
           microns.

4. · The membrane of claim 1 further
35   characterized in at least one of the following:
        a) the longitudinal axis of said pores is
           substantially perpendicular to said first face; or

b) the longitudinal axes of substantially all of said pores are substantially parallel.

5. The membrane of claim 1 further characterized in at least one of the following:
a) each face has substantially flat land areas; or
b) said first face has a surface porosity of at least about 5 percent; or
c) said first face has a surface porosity of at least about 20 percent; or
d) said first face has a surface porosity of at least about 40 percent.

6. The membrane of claim 1 further characterized in at least one of the following:
a) the major portion of the walls of each said pore are substantially parallel to the longitudinal axis of said pore; or
b) at least 50 percent of the length of the walls of said pores are parallel to the longitudinal axis of the pores; or
c) at least 75 percent of the length of the walls of said pores are parallel to the longitudinal axis of the pores; or
d) the cross-sectional areas of said pores are substantially uniform throughout at least 50 percent of the length of the longitudinal axes of said pores; or
e) the cross-sectional areas of said pores are substantially uniform throughout at least 75 percent of said longitudinal axes; or
f) at least 50 percent of the length of the walls of said pores are straight; or
g) at least 75 percent of the length of the walls of said pores are straight.

7. The membrane of claim 1 further characterized in that said pores extend completely

through said sheet from said first face to said second
face and the burst resistance of said membrane is
isotropic.

5   8.   The membrane of claim 1 further
characterized in at least one of the following:
       a) said pores have a pore size distribution of less ·
          than about 10 percent.
       b) the area of opening and spatial arrangement of
10   said pores is substantially uniform across said
          first face; or
       c) said pores extend completely through said sheet
          from said first face to said second face wherein
          and the cross-sectional areas of said pores are
15   substantially uniform throughout at least 50
          percent of the length of the longitudinal axes of
          said pores.

       9.   The membrane of claim 1 further
20   characterized in that said membrane further comprises
at least a second array of pores extending into said
sheet from said first face wherein substantially each
pore within said second array is individually
surrounded by a flat land area and the major portion of
25   the walls of each said pore are substantially parallel
to the longitudinal axis of said pore, said pores
having an average characteristic dimension of between
about 0.1 and about 5000 microns and a pore size
distribution of less than about 10 percent, the
30   longitudinal axes of said pores within said array being
substantially parallel with each other;
       wherein (1) at least one of said average
characteristic dimension, said pore size distribution,
depth, or shape of the pores of said second array is
35   different from said average characteristic dimension,
said pore size distribution, depth, or shape of the
pores of said first array; and/or (2) said longitudinal
axes of the pores of said second array is at least 5°

different from said longitudinal axes of the pores of
said first array.

        10. A membrane comprising a sheet having first
and second faces with pores extending into at least
said first face characterized in that the walls of each
said pore form a frustum-like shape, said pores having
an average characteristic dimension at their largest
end of between about 0.1 and about 5000 microns and a
pore size distribution at their largest end of less
than about 10 percent, the central axes of said pores
being substantially parallel.

        11. A method for making a membrane of claim 1,
characterized in that said method comprises:
        a) providing a mask comprising a sheet with an array
           of apertures therein, said apertures being of the
           desired shape and characteristic dimension of
           said pores and being arranged in the pattern in
           which said pores are desired;
        b) positioning said mask in close proximity with the
           first face of a film having two faces; and
        c) forming an array of pores simultaneously in said
           film by application of directional means for
           boring through said mask;
to yield said membrane.

        12. The method of claim 11 further
characterized in that said boring comprises application
of a collimated stream of reactive ions or collimated
energy beam through said mask.

        13. The method of claim 11 further
characterized in that said mask is generated while said
sheet is in direct contact with said film.

        14. The method of claim 13 further
characterized in that said mask is generated by:

a) applying a layer of resist material to said first
   face of said film;

b) imagewise exposing said layer of resist material
   with actinic radiation to differentially harden
   said resist material;

c) removing the unhardened areas of said layer of
   resist material, exposing first areas of said
   first face of said film;

d) applying a cap coating to said exposed areas of
   said first face of said film and the remaining
   portions of said layer of resist material; and

e) removing the remaining portions of said resist
   material and the cap coating thereon, thereby
   exposing second areas of said first face.

15. The method of claim 11 further
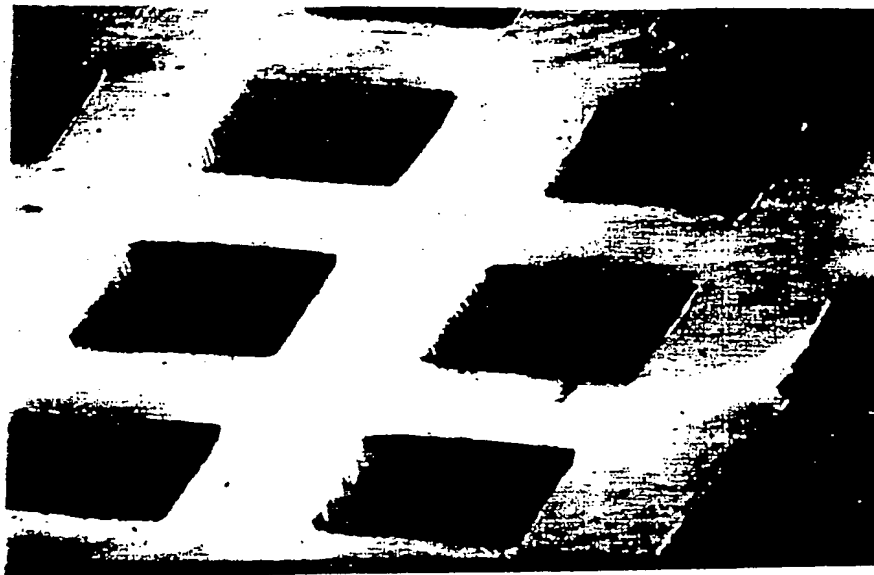characterized in that said imagewise exposing is
performed with laser interferometry.
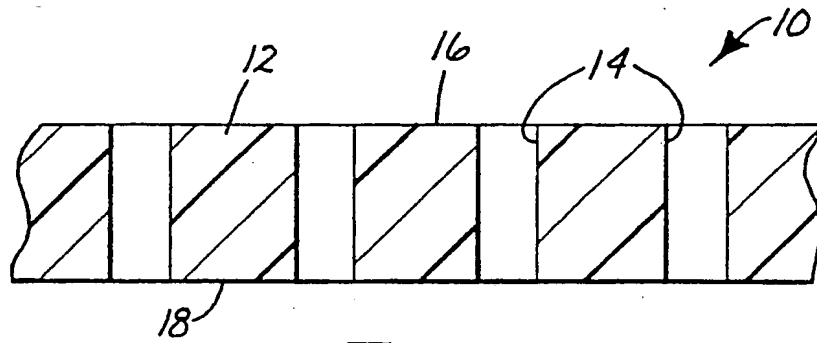
Fig 1
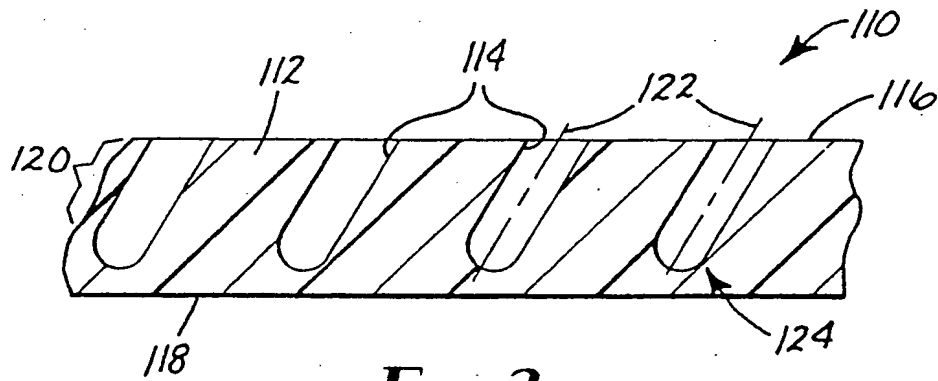
Fig 2
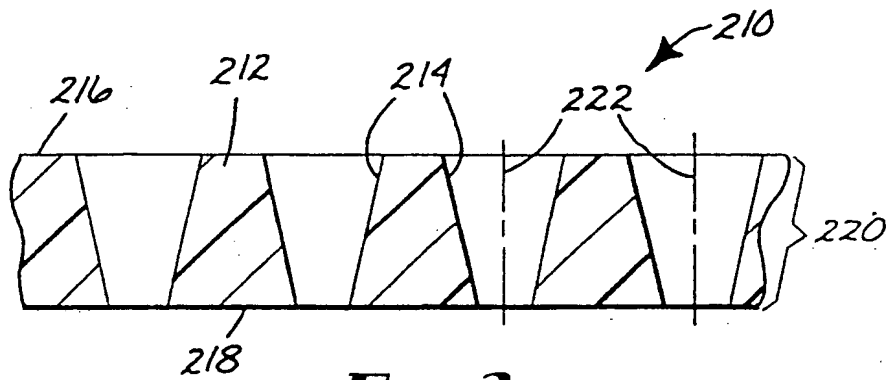
Fig. 3

Fig. 4

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Fig. 5A
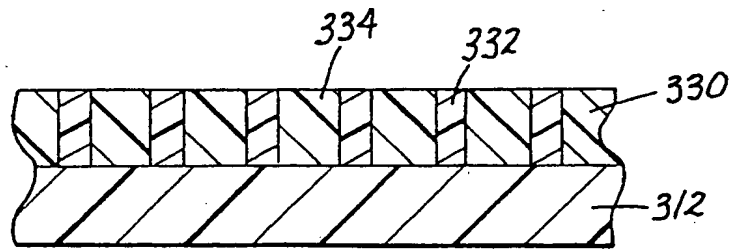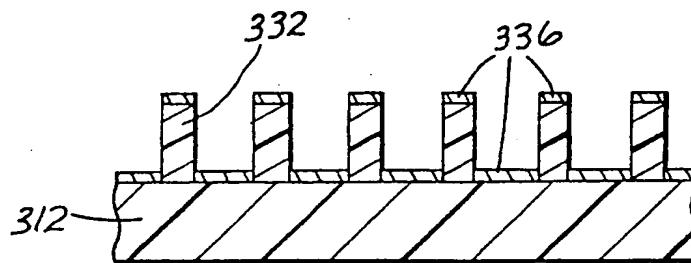
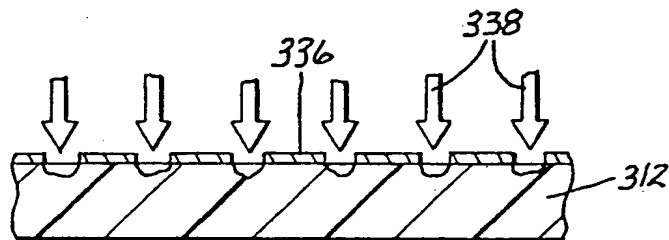Fig. 5B

Fig 5C

Fig. 5D

rnational application No.

PCT/US 92/09406

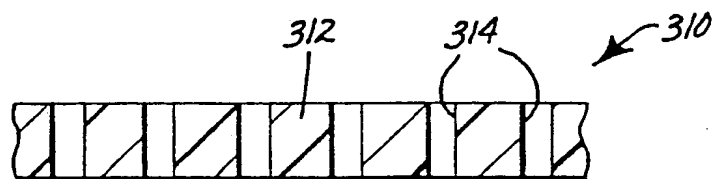## A. CLASSIFICATION OF SUBJECT MATTER

IPC5: B01D 69/02, B01D 67/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A1, 0459893 (CYCLOPORE S.A.), 4 December 1991 (04.12.91) --	1-15
A	US, A, 4923608 (T. FLOTTMANN ET AL), 8 May 1990 (08.05.90) -- --------	1-15

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" erlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 February 1993	12. 03. 93
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Authorized officer Britt-Marie Lundell

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A1- 0459893	04/12/91	CA-A-	2043624	02/12/91
		FR-A-	2662635	06/12/91
US-A- 4923608	08/05/90	DE-A-	3742770	29/06/89
		EP-A-	0325752	02/08/89
		JP-A-	2043927	14/02/90